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TRANSPARENT CUTTING OIL CONTAINING ACTIVE SULFUR AND SULFOCHLORINATED MONO-OLEFIN POLYMER

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This invention relates to a light colored or transparent cutting oil of the heavy duty type, and particularly to such an oil having a mineral lubricating oil base and containing the combination of both added active free sulfur and a sulfo-chlorinated mono-olefin polymer.

It is well recognized that cutting oils for heavy duty service can be prepared by sulfurizing mineral lubricating oils under rigorous conditions to provide a substantial content of highly active sulfur, but this results in a dark colored opaque oil which hides the work from the view of the operator during the cutting operation. Also, so-called transparent cutting oils have been produced by mildly sulfurizing mineral lubricating oil at temperatures of about 290–340° F. and at atmospheric presure to incorporate a lower content of added active sulfur in the oil, and then adding an extreme pressure agent, such as an aryl phosphate of the character of tricresyl phosphate. While such a cutting oil possesses a light color and sufficient transparency for clear observation of the work by the operator, it has proved incapable of handling certain heavy duty cutting operations. Consequently, it has been necessary to employ the opaque type of oil in these operations with resultant sacrifice in visual observation of the work. With the advent of improved harder alloys and higher cutting speeds in various precision cutting operations, the need for a truly transparent cutting oil of the heavy duty type which is substantially equivalent in cutting efficiency to the dark colored opaque oils has been emphasized.

A principal object of the present invention is to provide a transparent cutting oil of the heavy duty type employing a mineral lubricating oil base which approaches or substantially equals in cutting efficiency the previously used dark colored opaque oils.

A further object of the present invention is to produce such a transparent cutting oil of the heavy duty type while avoiding the use of expensive solvents or chemicals, whereby an economical product of superior quality is afforded.

In accordance with the present invention, the foregoing objects have been attained by incorporating in a refined mineral lubricating oil distillate of the character of a so-called pale oil, the combination of about 0.4–0.95% by weight of added active free sulfur, together with about 0.75–5% by weight of a sulfo-chlorinated mono-olefinic polymer having a substantial content of both combined chlorine and combined sulfur. It has been found that there is a cooperative or synergistic effect between these combined additives, with the net result that the transparent cutting oil provides superior performance in actual full scale cutting operations over transparent cutting oils heretofore available, and closely aproaches if not equals the cutting effectiveness of the heavy duty opaque oils. At the same time, the cutting oil of the present invention possesses a high transparency as represented by a light color on the Lovibond scale (½ in. cell) below 85.

The mineral lubricating oil employed as the base, and which constitutes at least about 95% by weight of the

composition, is a refined treated pressed distillate or dewaxed distillate, which is finished by stilling, light to moderate acid treating, neutralizing, steaming and brightening. A paraffin base oil is generally preferred. The oil has an SUS Viscosity at 100° F. of 100–200, and preferably about 110–170.

The added active free sulfur is introduced into the base oil by heating the latter with about 0.4–0.95% by weight of powdered sulfur at a temperature of about 290–340° F. for about ¾ to 1½ hours, and preferably at a temperature of around 315° F. for about 1 hour. The sulfur is believed to be mainly in solution in the oil, although it may be in a loosely combined form, such that the total added sulfur is in a highly active state. The amount of added sulfur is preferable toward the upper end of the aforesaid range, generally about 0.7–0.9% and approaches the limit of solubility of the sulfur in the particular base oil employed.

The introduction of the sulfur into the base oil can be accomplished by a batch treatment, or can be done in a continuous manner involving a pipe coil heating operation. The base oil with the added active sulfur preferably has a color on the Lovibond scale (½ in. cell) below about 40, and generally about 25–35, so that further darkening of the product upon the incorporation of the sulfo-chlorinated polymer will not raise the color of the finished oil above about 80–85, and preferably will be about 60 or lower. Following the sulfurization at the elevated temperature, the resulting oil is allowed to cool to about 150° F. or lower, and then air is bubbled through the oil or the latter is steam stripped under vacuum to remove H_2S until the sulfurized oil is no more than faintly positive to the lead acetate test. The sulfurized oil is then allowed to settle and the clear oil decanted. The sulfo-chlorinated polymer is added to the clear sulfurized oil at substantially room temperature.

The mono-olefinic polymers which are sulfo-chlorinated are those of the lower molecular weight olefins having less than 6 carbon atoms in the molecule, and include the liquid polymers of ethylene, propylene, the butylenes and the amylenes. The isobutylene polymers, such as diisobutylene and triisobutylene, are preferred. While the liquid polymers may be prepared from a single olefin, such as isobutylene, the copolymers formed by the polymerization of a mixture of two or more of the said lower molecular weight olefins, can also be employed. The polymerization is carried out in conventional manner in the presence of well-known catalysts, such as BF_3, solid phosphoric acid, aluminum chloride, sulfuric acid and the like. As hereinbefore stated, the polymerization is terminated before the resinous stage and while the polymers are liquid when cool.

The sulfo-chlorination of the resultant polymers is conveniently accomplished by reacting the same with about 40–50% by weight of sulfur mono-chloride without added heat, followed by subsequent stabilization of the reaction product by heat treatment at temperatures of about 300–350° F. This is followed by neutralization of any strong acidity so that the product passes the copper strip corrosion test at 122° F., the neutralization being conveniently accomplished by passing the sulfo-chlorinated polymer in contact with marble chips. In order to incorporate a higher proportion of chlorine with respect to sulfur in the polymer, the latter may be first chlorinated as by bubbling chlorine gas through material at 150° F., and the resulting chlorinated product subsequently treated with about 30–50% of sulfur monochloride and stabilized in the foregoing manner. The resulting sulfo-chlorinated mono-olefin polymers of this type generally contain about 15–30% by weight of combined chlorine and 10–25% by weight of combined sulfur.

A preferred material of this class is sulfo-chlorinated

diisobutylene containing about 19–22% of combined sulfur and 22–25% of combined chlorine. Another suitable material of this type is sulfo-chlorinated triisobutylene having approximately 14–17% of combined sulfur and about 19–22% of combined chlorine. "Anglamol 35" sold by the Lubrizol Corporation is representative of a commercially available material which is eminently satisfactory for purposes of the present invention, and is a sulfo-chlorinated diisobutylene containing 23–25% of combined chlorine and 19–22% of combined sulfur. Both the sulfur and chlorine are stably combined and the product is non-corrosive in the copper strip corrosion test at 122° F. such as to produce no blackening of the copper strip in 6 hours.

The sulfo-chlorinated polymer is added to the base oil in a proportion to provide about 0.75–5% by weight on the basis of the finished cutting oil, and preferably about 1.25–2.0% from the standpoint of color and cost. The addition is made by stirring the sulfurized base oil with the required amount of sulfo-chlorinated polymer at substantially atmospheric temperature, although it can be added at a mildly elevated temperature below about 150° F. While these sulfo-chlorinated mono-olefinic polymers are known extreme pressure agents, it was not to be anticipated that this type of material in combination with the added active free sulfur in the base mineral oil would provide a cutting oil having both the high transparency and the superior cutting efficiency in actual cutting operations. This is especially true since other known types of sulfo-chlorinated extreme pressure agents, such as sulfo-chlorinated fatty oils, failed to satisfy these requirements. Thus the sulfo-chlorinated fatty oils either produce darkening of the cutting oil so that transparency is lost, or else do not give the synergistic effect with the added active free sulfur such that the cutting properties are inferior.

The following examples are given in order to illustrate the present invention:

Example 1

A blend of 480 pounds of a refined paraffin base pale oil having an SUS viscosity at 100° F. of 230 with 320 pounds of a refined paraffin base pale oil having an SUS viscosity at 100° F. of 108.8 was charged to a steam heated kettle equipped with a stirrer. During heating of the kettle contents up to a temperature of 320° F., 27.7 pounds of the blend was removed to prevent overflow, leaving 773.3 pounds of the blend to be sulfurized. At this temperature of 320° F., 6.24 pounds of sulfur were slowly added with stirring, and the temperature was maintained at 310–320° F. for one hour. The steam to the kettle was then cut off, and cooling water supplied to the kettle jacket to cool the sulfurized oil down to a temperature of 150° F. in one hour. A control sample of the sulfurized oil had a color of 25 on the Lovibond scale (½" cell) and an SUS viscosity of 100° F. of 166. Air was then bubbled through the batch in the kettle for 3½ hours, until the latter was only slightly positive to the lead acetate test and a sample had a color on the Lovibond scale (½" cell) of 35. The batch was then allowed to stand until it cooled to room temperature and was then filtered through cheese cloth.

248.3 pounds of the foregoing sulfurized pale oil was charged to a kettle together with 11.7 pounds of a cutback consisting of a ⅓ part by weight of "Anglamol 35" and ⅔rds part by weight of a paraffin base lubricating oil distillate having an SUS viscosity at 100° F. of 230. The kettle contents were stirred for 45 minutes at room temperature. The resulting product which was a clear straw-colored mobile oil was then pumped to tankage and allowed to stand in quiescent condition for a period of about five weeks. It is found that any sedimentation will occur in this period, and the supernatant clear oil is then stable in subsequent storage and use. The foregoing finished oil had the following calculated composition:

	Percent by wt.
Pale oil	97.74
Added active free sulfur	0.76
"Anglamol 35"	1.5

The foregoing "Anglamol 35" tested 21.57% by weight of combined sulfur and 23.8% of combined chlorine. The following tests were obtained on the above finished oil:

Gravity ° API	26.1
Flash, O. Cleve., ° F	390
Fire, Cleve., ° F	455
SUS Vis. at 100° F	170.7
Color, Lovi. ½" cell	50
Carbon residue, percent	0.15
Total sulfur, percent	1.25
Cold test at 25–30° for 60 hours	[1] O. K.
SAE extreme pressure, 1000 R. P. M.-lbs.	166, 161, 152

[1] No sedimentation.

The foregoing SAE extreme pressure test represents a laboratory bench test which has been found to correlate about as well as any extreme pressure test with actual field tests in full scale cutting operations. However, even this bench test is incapable of distinguishing between effective heavy duty cutting oils; and field tests in full scale cutting operations are required to prove the merits of a cutting oil of this character.

Example 2

A series of transparent cutting oils were prepared in the manner of Example 1 above, but employing different proportions of "Anglamol 35." Tests obtained on these oils are set forth in the following Table II:

	Sulfurized Base Oil+ Additive, percent by wt.	Color Lovibond, ½ in. cell	SAE Test, 1,000 R. P. M., lbs.
1		40	55
2	[1] 3.0	60	250
3	[1] 4.0	70	280
4	[1] 5.0	75	550+
5			60
6	3.0	70	233
7	4.0	80	357
8	5.0	85	550+
9		45	203
10	1.0		173
11	2.0	65	550+
12	3.0	75	550+
13	4.0	80	550+
14	5.0	85	550+
15		30	70
16	1.5	50	166

[1] Also contains 1% tricresyl phosphate.

Samples 1, 5, 9 and 15 of the above table represent different batches of sulfurized base oil which may vary materially in SAE value as shown. The samples immediately following each base oil were prepared from that particular batch. Samples 2–4 inclusive also contained 1% by weight of tricresyl phosphate in the formulation. Comparison of samples 3 and 7 indicates that tricresyl phosphate is not compatible with the sulfo-chlorinated polymer in this type of cutting oil and is desirably omitted from the formulation. Samples 8 and 14 show that 5% of the sulfo-chlorinated polymer represents about the upper limit in order to obtain the desired transparency and color.

Example 3

The transparent cutting oil of Example 1 above was subjected to field tests in a push rod threading operation in comparison with the previously known type of transparent cutting oil containing tricresyl phosphate, and with a dark colored highly sulfurized heavy duty cutting oil of known superior cutting properties. The operation

involved the use of a Landis single head threading machine in forming a ⅝ in. by No. 18 thread, 3 in. long at a cutting speed of 60–63 feet per minute on push rods made of SAE 4140 steel. In this test, 500 to 550 push rods were satisfactorily threaded with the transparent cutting oil of the present invention before it became necessary to regrind the chasers, as compared to 200–250 for the former type of transparent cutting oil and 700–750 for the dark colored heavy duty cutting oil. Thus the cutting oil of the present invention more than doubled the prior output with a transparent cutting oil, and approached in cutting effectiveness the output of an opaque heavy duty cutting oil that prevented the work from being visually observed.

Example 4

The transparent cutting oil of Example 1 above was cut back 50% with pale oil to provide a product having approximately 0.4% of added free active sulfur and 0.75% of "Anglamol 35." This cutting oil was subjected to field tests in a threading operation on No. 4140 heat treated steel in comparison with the opaque type of highly sulfurized heavy duty cutting oil. The operation was carried out on a Landis Double Head Threading Machine cutting ⅝ in. No. 11 pitch threads throughout a length of 13 ft. on each of the steel bars at a spindle speed of 195 R. P. M. and a surface speed of 65 feet per min. The transparent cutting oil of the present invention gave an average of 19 bars satisfactorily threaded before the chasers required removal for regrinding, in comparison to an average of 18 bars for the dark colored heavy duty oil.

Example 5

The cutting oil of Example 1 above was subjected to field tests in a hobbing operation in comparison with both the previously used type of transparent cutting oil containing tricresyl phosphate, and the dark colored highly sulfurized heavy duty type of cutting oil. This operation involved use of a Barber-Coleman Hobber cutting ten SAE 4027 steel spur gears at a time at a speed of 165 feet per minute on a 6 in. diameter 5 thread hob. In a five months test, the transparent cutting oil of the present invention was rated comparable to the dark colored heavy duty cutting oil, while the previously known transparent cutting oil was found to be incapable of satisfactorily handling this severe cutting operation.

Example 6

The following illustrates continuous manufacture of the cutting oil of the present invention. A pale oil blend having an SUS viscosity at 100° F. of 125–130 for a lighter grade and 160–165 for a heavier grade was charged to a heater and reactor unit consisting of a pipe coil heater and tank with recirculating pump. After this system was filled with approximately 120 bbls. of the pale oil blend, the contents were recirculated in the system at the rate of 50 bbls. per hour until the outlet temperature of the reactor had been raised to 325–335° F. Sulfur was then added to the oil in the system at the rate of 125 pounds per hour, while recirculating was continued and the reactor outlet temperature maintained at 325–335° F., until a quantity of sulfur sufficient to provide 0.8% by weight based on the final composition and represented by the oil then in the system had been added. At this time, recirculation was stopped and a continuous operation involving pumping the oil through the heater and

reactor and then discharging was initiated. With the charge pump set for 50 bbls. per hour, sulfur was injected into the charge oil at the rate of 125 pounds of sulfur per hour, while both the preheater and reactor outlet temperatures were maintained at 325–335° F. The oil required about 45–60 min. to traverse this system.

The sulfurized oil was discharged into a previously evacuated vacuum tower into which steam was injected to remove H_2S. The oil from the tower then passed through a cooler maintained at an outlet temperature of 120–140° F. to a large finishing tank. Then 1.5% by weight of "Anglamol 35" (or 4.5% of the cutback of Anglamol 35 containing twice its weight of pale oil) was added and blended by air blowing for about 30 min. The resulting cutting oil was then allowed to stand in tankage for about 5 weeks, and the supernatant oil was then filled into containers through a 150 mesh screen.

In order to prepare a still lighter grade of the present transparent cutting oil, the foregoing finished cutting oil prepared from the light blend as described above can be cut back with additional pale oil to the desired extent, such as about 50%.

Obviously, many other modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A transparent cutting oil consisting essentially of a mineral lubricating oil distillate having an SUS viscosity at 100° F. of 100 to 200 containing 0.4 to 0.95 percent by weight of added active free sulfur incorporated in the mineral oil at a temperature of about 290–340° F., and 0.75 to 5% by weight of sulfurized and chlorinated diisobutylene containing 23–25 percent of combined chlorine and 19–22 percent of combined sulfur, said sulfurized and chlorinated diisobutylene being non-corrosive to copper in the copper strip corrosion test, such as to produce no blackening of the copper strip at 122° F. for six hours, said cutting oil having a color on the Lovibond scale (½ inch cell) below 85 and a cutting effectiveness at least approaching that of a dark colored opaque more highly sulfurized heavy duty cutting oil.

2. A transparent cutting oil consisting essentially of a refined paraffin base mineral lubricating oil distillate having an SUS viscosity at 100° F. of 100–200 containing about 0.7–0.9% by weight of added active free sulfur incorporated in the mineral oil at a temperature of about 300–335° F., and about 1.25–2.0% by weight of a sulfurized and chlorinated diisobutylene having 23–25% of combined chlorine and 19–22% of combined sulfur, said cutting oil having a color on the Lovibond scale (½ inch cell) below 80.

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